Effects of Increasing Potassium Chloride and Calcium Chloride Ionic Strength on Pesticide Sorption by Potassium- and Calcium-Smectite

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ABSTRACT

In aqueous suspension, the affinity of many pesticides for smectites is influenced by the clay properties such as surface area, surface charge density and location, exchangeable cations, and hydration status of exchangeable cations in clay interlayers. The amount and the type of salts present in the aqueous phase influence clay quasicrystal structures and hydration status, which we hypothesize as major determinants of pesticide sorption. To test this hypothesis, we measured sorption isotherms of alachlor, atrazine, dichlobenil, and diuron by K^+–saturated smectite (K-SWy-2) in KCl solution and Ca^{2+}–saturated smectite (Ca-SWy-2) in $CaCl_2$ solution at several ionic strengths. The results indicated that pesticide sorption by K-SWy-2 significantly increased with increasing aqueous KCl concentration. In contrast, sorption by Ca-SWy-2 at different $CaCl_2$ ionic strengths remained nearly constant. The "salting-out" effect on the reduction of dissolution of pesticides failed to account for the significantly increased sorption by K-SWy-2 in aqueous KCl solutions. We conclude that formation of better-ordered clay quasicrystals and shrinkage of clay interlayer distance owing to increased KCl ionic strength facilitate the intercalation of pesticides leading to greater sorption by the clay, while the salting-out effect plays a minor role (if any) in the observed sorption enhancement.

S ORPTION TO SOILS and sediments is a major factor influencing transport, bioavailability, and hence fate of pesticides in the environment. A widely accepted view is that soil organic matter (SOM) functions as the predominant sorptive phase whereas soil mineral fractions play a relatively minor role in the sorption of neutral organic contaminants and pesticides from water (Chiou et al., 1979; Chiou et al., 1983; Karickhoff et al., 1979; Kile et al., 1995; Weber and Huang, 1996; Xia and Ball, 1999; Xing and Pignatello, 1997). This view is exemplified by the reliance on soil organic carbon-normalized sorption coefficients (K_{OC}) to predict the fate and transport of organic compounds in soils. However, several recent studies and a few earlier ones provide clear evidence that soil minerals can function as effective adsorbents for pesticides and organic contaminants under environmentally relevant conditions (Bailey et al., 1968; Bowman, 1973; Boyd et al., 2001; Celis et al., 1998; Haderlein et al., 1996; Hundal et al., 2001; Johnston et al., 2002; Laird et al., 1992; Mortland, 1970; Sheng et al., 2002; Zhu et al., 2004). For important categories of pesticides (e.g., triazines, carbamates, ureas, nitrophenols, benzonitrile) and organic contaminants (e.g., nitro-aromatics), sorption by clays can be equal or greater than that by SOM based on comparisons of sorption by a unit mass of isolated clay minerals vs. SOM and by synthetic clay–organic matter complexes (Li et al., 2003; Sheng et al., 2001). Mineral fractions in soils can also function as effective adsorptive domains for pesticides and organic contaminants, particularly for the soils containing smectite clays (Charles et al., 2006).

Among the naturally occurring soil minerals examined, smectite clays manifested the greatest sorption (on unit mass of sorbent basis) for nitroaromatic compounds due to their large surface areas and expandability (Weissmahr et al., 1998). Among smectites, less surface-charge-density clays typically provide larger hydrophobic nanosites on siloxane surface between exchangeable cations for adsorption leading to greater uptake (Jaynes and Boyd, 1991; Laird et al., 1992; Lee et al., 1990; Sheng et al., 2002). The origin of negative charges in smectite clays also affects pesticide sorption. Negative charges arising from tetrahedral sheet isomorphic substitution are more localized, which appears to have a favorable effect on the interlayer environment for pesticide sorption compared to smectites with isomorphic substitution predominantly in the octahedral sheet (Aggarwal et al., 2006).

The neutral siloxane surfaces of smectite clays are important adsorption domains for organic compounds; however, water molecules associated with exchangeable cations and clay surfaces may obscure these sites. Organic compounds must be able to effectively compete with these water molecules to access the mineral sorptive sites. The type of exchangeable cation strongly influences the hydration status of clay minerals. Among the inorganic cations commonly occurring in natural environments, less strongly hydrated cations (e.g., K^+) manifest smaller hydration spheres than more strongly hydrated cations (e.g., Ca^{2+}) hence leaving more neutral clay siloxane surfaces available for adsorption (Li et al., 2003, 2004a). Weakly hydrated cations also facilitate adsorption by easing the displacement of hydration waters thereby promoting solute interactions with exchange cations (e.g., formations of inner- and outer-sphere complexes) (Boyd et al., 2001). In addition, the basal spacings of more weakly hydrated cation-exchanged smectites, for example, K-smectite, often approximate the thickness of aromatic molecules such as nitroaromatic compounds. For example, K-smectite with sorbed

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Abbreviations: Ca-SWy-2, Ca^{2+}–saturated Wyoming montmorillonite reference smectite; CEC, cation exchange capacity; HPLC, high-performance liquid chromatography; K-SWy-2, K^+-saturated Wyoming montmorillonite reference smectite; SOM, soil organic matter; SWy-2, Wyoming montmorillonite reference smectite; XRD, X-ray diffraction.

pesticide (e.g., 2,4-dinitro-o-cresol) manifests a basal spacing of ~12.3 Å indicating that pesticide molecules align parallel to clay siloxane layers (Li et al., 2003; Sheng et al., 2001). This optimal configuration allows pesticides direct contact with siloxane surfaces thereby minimizing hydration of the pesticide; both are energetically favorable processes (Li et al., 2004a; Sheng et al., 2001). Ca-smectites, however, cannot attain this sorption configuration because they always expand to 15 Å or more in the presence of water, and it is comparatively more difficult to replace the strongly held waters associated with exchangeable Ca^{2+} on clay surfaces.

Pesticide sorption is influenced not only by intrinsic properties of smectite clays and exchangeable cations but also by physicochemical processes that impact the clay quasicrystal structures and interlayer environment. Smectites exist as quasicrystals in aqueous suspensions consisting of stacks of several to hundreds of clay platelets. Exchangeable cations compensating smectite negative charges possess different energies of hydration, which strongly influence the extent of interlayer swelling and size of quasicrystals. Many natural processes, such as cation exchange and wetting-and-drying cycling, cause changes in clay swelling and clay quasicrystal structures, which may affect pesticide sorption. Li et al. (2004b) noted that K^+–Ca^{2+} exchange reactions alter the extent of pesticide sorption by destroying and reforming clay quasicrystal structures. The larger hydrated cation Ca^{2+} broke clay stack structures and forced clay interlayers open in the process of replacing the relatively smaller hydrated K^+ cations. This cation exchange process produces unfavorable pesticide sorptive domains (i.e., those saturated with Ca^{2+}) in clay interlayers. Wetting-and-drying cycles can also influence pesticide sorption. Chappell et al. (2005) observed a much greater sorption of atrazine by air-dried K-smectite relative to that by K-smectites that had never been dried. They concluded that wetting-and-drying process altered interlayer hydration and swelling status thereby influencing pesticide affinity with smectites.

Smectite quasicrystal structures and hydration status are also influenced by the amount and the type of salts including those present in aqueous phase and those compensating clay negative-charged sites determine swelling status by influencing the orientation of clay platelets and interlayer hydration (Low, 1980; McBride, 1994; Zhang et al., 1995). Clay platelets tend to align parallel and form quasicrystals in aqueous solution at high salt concentrations. In addition, the increased ionic strength may reduce the distance between clay platelets. These factors may in turn facilitate the intercalation of pesticides. Most previous studies ignored the effects of salt concentrations on clay mineral structures and its relation to pesticide sorption, or assumed that sorption was influenced only by the salting-out effect of electrolytes that slightly diminishes the solubility of pesticides in aqueous solution. The objective of this study was to evaluate the influence of ionic strength–induced alterations of smectite structures on the sorption of pesticides. To achieve this objective, we measured sorption of four pesticides (a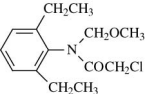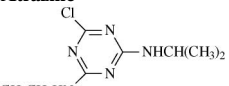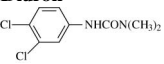lachlor, atrazine, dichlobenil, and diuron) by K- and Ca-saturated smectite clays from water at several KCl and $CaCl_2$ ionic strengths. The results help reveal the influence of electrolytes on the clay interlayer environment and hence further elucidate the interaction mechanisms of pesticides with clay minerals in aqueous solution.

MATERIALS AND METHODS

Alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)-acetamide] and atrazine (6-chloro-N^2-ethyl-N^4-isopropyl-1,3,5-triazine-2,4-diamine) were purchased from ChemService Inc. (West Chestnut, PA) with a reported purity >99%. Dichlobenil (2,6-dichlorobenzonitrile) and diuron [N'-(3,4-dichlorophenyl)-N,N-dimethylurea] were purchased from Aldrich Chemical Company Inc. (Milwaukee, WI) with a reported purity >97%. Molecular structures and selected physical and chemical properties of these pesticides are listed in Table 1. Calcium chloride dihydrate (purity > 99%), potassium chloride (purity > 99%), and methanol (HPLC grade) were purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ) and used as received.

A reference smectite clay (SWy-2) was purchased from the Source Clays Repository of the Clay Minerals Society (Department of Agronomy, Purdue University, West Lafayette, IN). SWy-2 is a relatively low-charged smectite with negative charges arising primarily from isomorphic octahedral substitution. It has a cation exchange capacity of 82 $cmol_C$ kg^{-1} and a surface area of 750 m^2 g^{-1} (van Olphen and Fripiat, 1979). The <2-μm clay-sized fraction was collected by sedimentation, and cation-exchangeable sites were saturated with K^+ or Ca^{2+} by mixing with 0.5 M KCl or $CaCl_2$ solutions. Approximately 5 g of clay-sized fraction was mixed with 200 mL of 0.5 M KCl or $CaCl_2$ electrolyte solution in a 250-mL polyethylene bottle, and shaken at 120 rpm for ~8 h, then the clay suspension was centrifuged at 3295 g for 30 min, and the supernatant was discarded. This procedure was repeated four times. The excess KCl or $CaCl_2$ was removed by washing the clay suspensions with Milli-Q water until Cl^- was absent as determined by AgCl precipitation with $AgNO_3$. The clay suspensions were then quick-frozen, freeze-dried and stored in closed containers

Table 1. Molecular structures and selected properties of pesticides investigated.

Pesticides	Molecular weight†	Aqueous solubility†	n-Octanol-water distribution coefficients†
	g mol^{-1}	mg L^{-1}	log K_{OW}
Alachlor	269.77	242	2.64, 2.90
Atrazine	215.68	33	2.33–2.80
Dichlobenil	172.02	25	2.90
Diuron	233.11	40	1.97–2.81

† **Data from Montgomery (1997).**

before use. The detailed procedures of preparing clays can be found in Arroyo et al. (2005). Homoionic K^+– and Ca^{2+}–saturated smectite clays are hereafter referred to as K-SWy-2 and Ca-SWy-2, respectively.

Pesticide sorption isotherms by K-SWy-2 from aqueous KCl solutions and by Ca-SWy-2 from aqueous $CaCl_2$ solutions were measured using a batch equilibration method. A series of initial pesticide concentrations were prepared using either aqueous KCl solutions (0.01, 0.05, 0.10, 0.20, and 0.30 M) or $CaCl_2$ solutions (0.005 and 0.10 M). The initial pesticide concentrations used in this study were 0 to 80 mg L^{-1} for alachlor, 0 to 25 mg L^{-1} for atrazine, 0 to 20 mg L^{-1} for diuron, and 0 to 18 mg L^{-1} for dichlobenil. The upper limit of the range was between 0.3 to 0.75 times the aqueous solubility. K-SWy-2 or Ca-SWy-2 clays were weighed into glass centrifuge tubes, the initial solutions were added, and the tubes were closed with Teflon-lined screw caps. The tubes were then rotated end-over-end (40 rpm) for 24 h at room temperature (23 ± 2°C), followed by centrifugation at 2600 g for 30 min. Previous studies indicated that sorption equilibrium was reached within this period of contact time (Sheng et al., 2001; Sheng et al., 2002). Supernatants were sampled and analyzed for pesticide concentrations using a PerkinElmer high-performance liquid chromatography (HPLC) consisting of a Binary 250 LC pump, a Series 200 autosampler, and a Series 200 UV-visible detector (Perkin-Elmer, Norwalk, CT). An Alltech platinum extended polar selectivity (EPS) C18 column (15 cm by 4.6 mm i.d.; Alltech Assoc. Inc., Applied Science Labs, Deerfield, IL) was used in HPLC analysis. The UV-visible detector absorption

wavelength was set at 225 nm for alachlor, 230 nm for atrazine, 238 nm for dichlobenil, and 250 nm for diuron. The mobile phase composition was an isocratic mixture of methanol and water, which was optimized for each pesticide. The mobile phase flow rate was set at 1.0 mL min^{-1}. Experimental controls consisted of the initial pesticide solutions in the supporting electrolyte without clay. No changes in pesticide concentrations were detected in the controls during the experimental equilibration period. Sorbed pesticide concentrations were then calculated from difference between the initial and equilibrium solution phase concentrations.

RESULTS AND DISCUSSION

Sorption isotherms of alachlor, atrazine, dichlobenil, and diuron by K-SWy-2 from 0.01, 0.05, 0.10, 0.20, and 0.30 M KCl aqueous solutions are presented in Fig. 1. Sorption isotherms for atrazine, dichlobenil, and diuron were nonlinear with the curvature concave to the abscissa (L-type), indicating a site-limiting sorption process. In contrast, sorption of alachlor displayed an upward S-type isotherm, that is with curvature convex to the abscissa. This type of sorption isotherm suggests cooperative sorption in which weak pesticide–clay interactions are presumed to occur at low aqueous concentration, whereas at higher aqueous concentrations the sorbed pesticide promotes further sorption due possibly to the creation of additional sorptive sites through a better
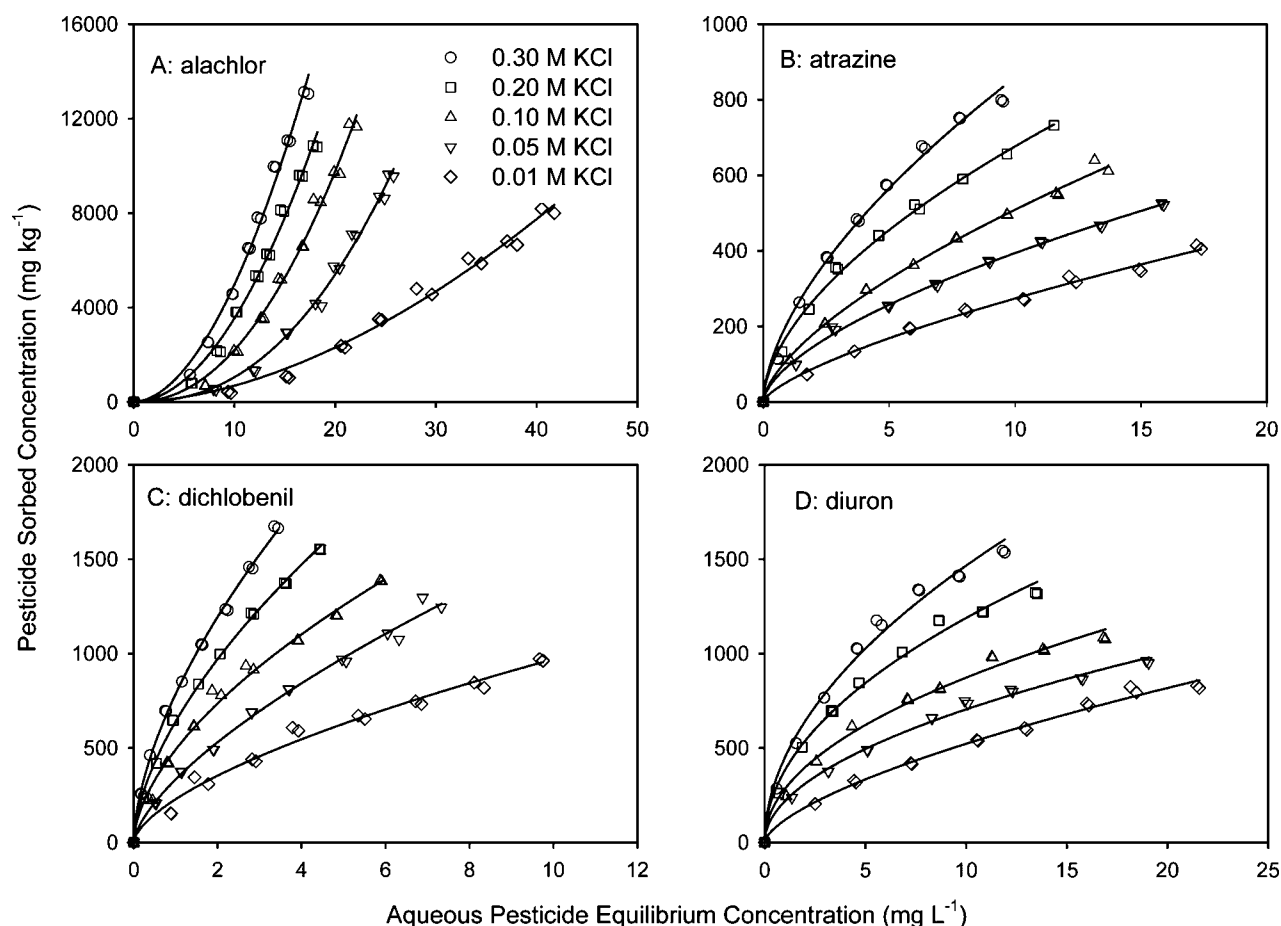

Fig. 1. Sorption isotherms of (A) alachlor, (B) atrazine, (C) dichlobenil, and (D) diuron by K^+–saturated smectite (K-SWy-2) at several KCl ionic strengths.

alignment of clay platelets (Li et al., 2004b) and/or condensation of organic compounds in clay interlayers (Hundal et al., 2001). This upward S-type isotherm is also commonly observed in pesticide sorption by clay minerals such as Ca- and Al-smectites (Li et al., 2003; Sawhney and Singh, 1997; Sheng et al., 2002).

All sorption isotherms were fit to the Freundlich equation: $Q = K_f C^n$ in which Q (mg kg^{-1}) is the amount of pesticide sorbed by clay; C (mg L^{-1}) is the equilibrium aqueous concentration of pesticide; K_f (mg^{1-n} L^n kg^{-1}) is Freundlich sorption coefficient, and n (unitless) is a describer of isotherm curvature. Freundlich equation fittings are shown as the solid lines in Fig. 1 with the parameters listed in Table 2. The results indicate that the Freundlich equation well described sorption by SWy-2 for the pesticides examined in this study (r^2 values > 0.99).

In Fig. 1, it is apparent that pesticide sorption increased with increasing KCl concentration in aqueous solution. To further quantify the impact of electrolyte concentration or ionic strength (I) on sorption enhancement, pesticide sorption coefficients (i.e., clay-sorbed concentration divided by aqueous equilibrium concentration) at the relative concentration of 0.05 were normalized to the corresponding sorption coefficients by K-SWy-2 in 0.30 M KCl solution (584 L kg^{-1} for alachlor, 175 L kg^{-1} for atrazine, 720 L kg^{-1} for dichlobenil, and 320 L kg^{-1} for diuron). The relative concentration is the pesticide aqueous equilibrium concentration relative to the aqueous solubility. The relative sorption coefficients were plotted against KCl ionic strength in aqueous solution (Fig. 2). Compared with the sorption in 0.01 M KCl solution at the relative aqueous pesticide concentration of 0.05, the sorption of atrazine, dichlobenil, and diuron increased by factors of approximately 1.5, 2.0, 3.0, and 3.5 times as KCl concentration increased to 0.05, 0.10, 0.20, and 0.30 M. The upward S-type isotherm for alachlor resulted in a more abrupt increase in sorption; sorption coefficients were 1.7 times (0.05 M KCl), 3.5 times (0.10 M KCl), 5.4 times (0.20 M KCl), and 7.4 times (0.30 M KCl) more than that in 0.01 M KCl solution at alachlor concentration of 12 mg L^{-1} (relative concentration of 0.05).

We hypothesize that enhanced pesticide sorption is due to alterations in the quasicrystal structures and swelling status of K-SWy-2 arising from the presence of different KCl concentrations. Specifically, increased KCl
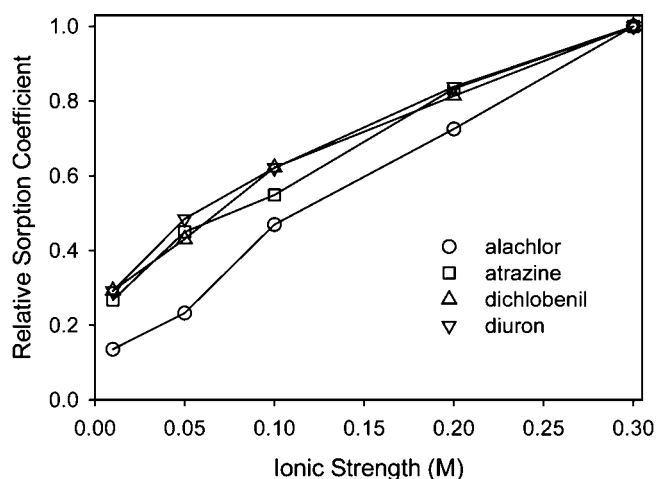

Fig. 2. Pesticide sorption coefficients normalized to the sorption by K$^+$–saturated smectite (K-SWy-2) from 0.30 M KCl solution at the aqueous relative concentration of 0.05 as a function of ionic strength.

ionic strength causes the clay platelets to form better-ordered parallel configurations and simultaneously reduces the amount of water in the clay interlayers; both processes facilitate the intercalation of pesticides in clays. In aqueous solution, clay particles usually exist as quasicrystals consisting of a stack of platelets with the structures and orientations significantly influenced by the amount and the type of salts present in the aqueous solution. To investigate the configurations of clay quasicrystals, we previously recorded X-ray diffraction (XRD) patterns for K-SWy-2 suspension at each KCl concentration (detailed by Li et al., unpublished data, 2006). The results showed that KCl concentration ≥ 0.1 M caused K-SWy-2 to form quasicrystal structures with a basal spacing of ~15.5 Å, which indicates two layers of water molecules in the interlayers domains. In 0.05 M KCl, a weak 15.5-Å XRD peak was observed indicating that only small or highly disordered quasicrystals were formed. In 0.01 M KCl, the clay platelets were randomly distributed in solution as no apparent XRD peak was observed.

When smectite is suspended in a salt solution, diffuse double layers form in the region adjacent to the external surfaces of the quasicrystals, which help keep the smectite quasicrystals suspended because an osmotic swelling pressure develops whenever two quasicrystals approach close enough for their diffuse double layers to overlap

Table 2. Sorption isotherm fitting parameters for pesticides by K$^+$–saturated smectite (K-SWy-2) and Ca^{2+}–saturated smectite (Ca-SWy-2) in KCl and CaCl$_2$ solutions at several ionic strengths.

Electrolyte concentration	Alachlor			Atrazine			Dichlobenil			Diuron		
	K_f	n	r^2	K_f	n	r^2	K_f	n	r^2	K_f	n	r^2
						K-SWy-2						
0.01 M KCl	12.2	1.75	0.988	54.5	0.701	0.995	229	0.627	0.985	119	0.647	0.994
0.05 M KCl	4.46	2.37	0.993	95.6	0.615	0.998	334	0.667	0.994	218	0.510	0.995
0.10 M KCl	15.6	2.15	0.991	115	0.645	0.997	492	0.582	0.992	283	0.490	0.991
0.20 M KCl	39.7	1.95	0.992	181	0.573	0.998	641	0.600	0.998	381	0.494	0.992
0.30 M KCl	68.5	1.86	0.992	214	0.603	0.994	787	0.603	0.998	448	0.515	0.991
						Ca-SWy-2						
0.005 M CaCl$_2$	4.38	2.21	0.992	7.29	0.997	0.999	10.0	0.895	0.992	17.1	0.797	0.996
0.10 M CaCl$_2$	9.51	2.11	0.994	8.39	0.966	0.995	7.89	0.951	0.998	15.9	0.832	0.994

(McBride, 1994). The nature of water in interlayers within quasicrystals is very different from that of water in diffuse double layers adjacent to external surfaces of quasicrystals; the interlayer water is highly polarized by the close proximity of the interlayer cations and surface charge site (Sposito and Prost, 1982). At a low salt (KCl) concentration a relatively larger quasicrystal can split into two or more smaller quasicrystals, which diminishes the interlayer surface area and increases external surface area. Our previous work (Boyd et al., 2001) has shown that pesticides are preferentially sorbed in interlayer domains due to the subaqueous nature of the interlayer environment. Thus the primary impact of decreasing ionic strength on pesticide sorption affinity of K-SWy-2 is believed to be related to the breakup of quasicrystals and correspondingly loss of 15.5 Å interlayer domains, which has been confirmed by XRD patterns (Li et al., unpublished data, 2006). In contrast, increasing KCl ionic strength diminishes the energy barrier that stabilizes the 15.5 Å interlayer domains (Laird, 1996) thus potentially allowing some interlayer domains to collapse to the energetically more favorable 12.3 Å basal spacing as pesticide is adsorbed.

In contrast to the significantly enhanced pesticide sorption by K-SWy-2 with increasing KCl concentration, changes of $CaCl_2$ solution concentration (0.005 and 0.10 M) have little effect on pesticide sorption by Ca-SWy-2 (Fig. 3). Sorption of alachlor by Ca-SWy-2 displayed an upward curving (S-type) isotherm that is similar to sorption by K-SWy-2. The sorption pattern for atrazine, dichlobenil, and diuron demonstrated essentially linear (C-type) or slightly concave downward (L-type) isotherms. The Freundlich equation was used to fit the sorption isotherms (solid lines in Fig. 3) and sorption parameters are reported in Table 2. Calculations using the fitting parameters to quantitatively compare the sorption at the two $CaCl_2$ concentrations indicate that sorption from 0.10 M $CaCl_2$ is approximately 1.7 (alachlor), 1.1 (atrazine), 0.87 (dichlobenil), and 0.99 (diuron) times the corresponding sorption from 0.005 M $CaCl_2$ solution. Ionic strength has little effect on pesticide sorption by Ca-SWy-2 in $CaCl_2$ solutions due principally to the nature of water associated with Ca-SWy-2. Ca-SWy-2 is hydrated with two layers of interlayer water under ambient air-dried conditions (basal spacing ~15 Å) and four water layers in aqueous solution (basal spacing of ~20 Å), which is independent of $CaCl_2$ ionic strength over a large range (McBride, 1994). In addition, the hydration enthalpy of Ca^{2+} is −1580 kJ mol^{-1}, five times greater than K^+ (−314 kJ mol^{-1}). The greater hydration energy results in more strongly held water molecules in the hydration sphere of Ca^{2+}, which inhibits the dehydration of pesticides by replacing interlayer waters as well as the development of strong inter-
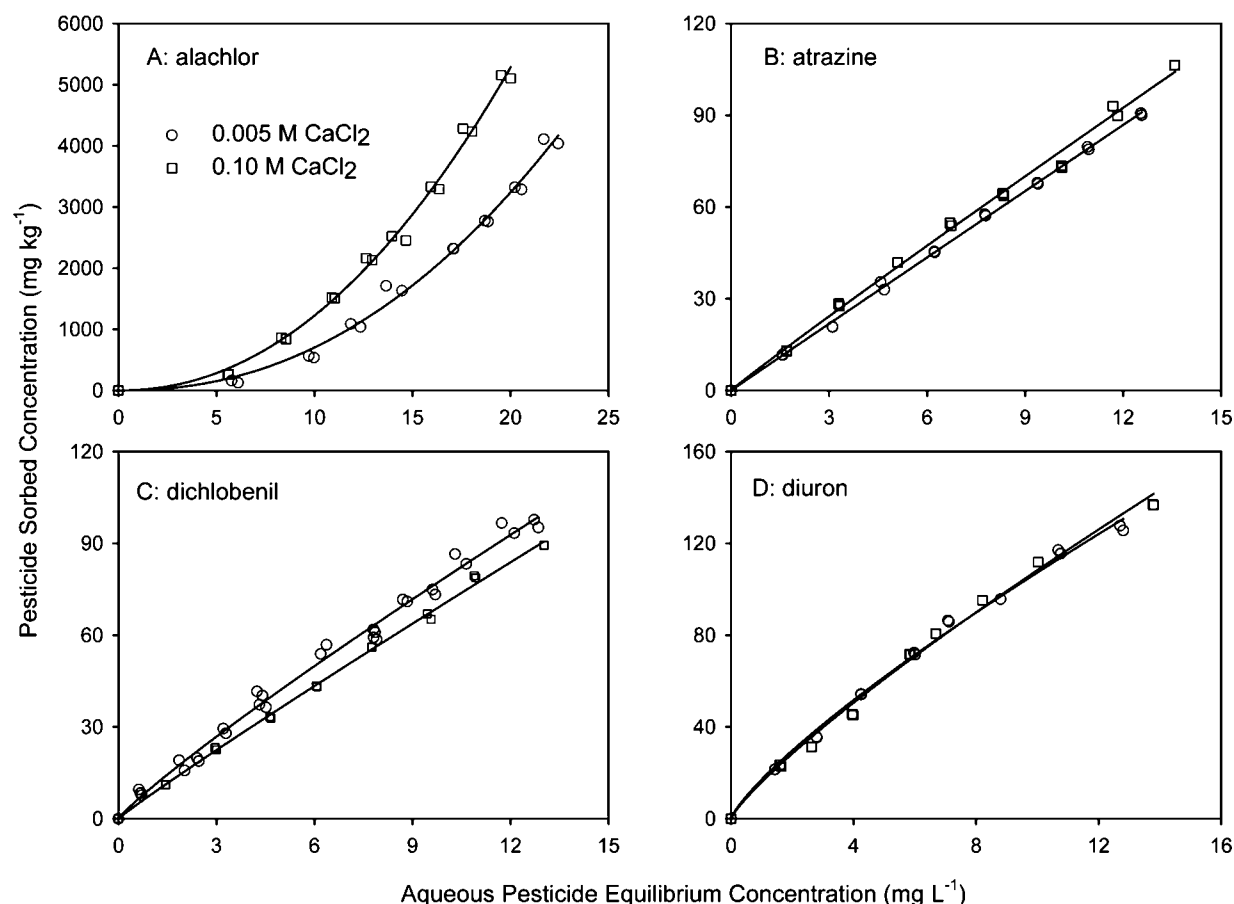

Fig. 3. Sorption isotherms of (A) alachlor, (B) atrazine, (C) dichlobenil, and (D) diuron by Ca^{2+}–saturated smectite (Ca-SWy-2) in 0.005 M and 0.10 M $CaCl_2$ solutions.

actions between polar functional groups of pesticides and Ca^{2+}. Compared with K-smectites, the larger interlayer distance of Ca-SWy-2 and strong hydration of Ca^{2+} impede the direct contact of pesticide aromatic rings with the opposing clay siloxane surfaces thereby manifesting a relatively lower adsorption (Li et al., 2004a; Sheng et al., 2002). This explanation is consistent with the greater sorption of atrazine, dichlobenil, and diuron by K-SWy-2 observed for K-SWy-2 than Ca-SWy-2. However, at low ionic strength (KCl = 0.01 M) alachlor sorption by K-SWy-2 was close to that by Ca-SWy-2 in 0.01 M $CaCl_2$, which is plausibly owing to the bulk substituents on the aromatic ring of alachlor, and poorly parallel order of K-SWy-2 clay platelets in a low ionic-strength solution (Li et al., unpublished data, 2006).

Sorption of hydrophobic organic contaminants by soils and sediments has been noted to increase with increasing aqueous salinity (e.g., seawater). High concentration of salts in solution reduces aqueous solubility of organic compound (the salting-out effect) or possibly alters dissolved organic matter configurations, leading to enhanced sorption for strongly hydrophobic compounds (e.g., polycyclic aromatic hydrocarbons) (Brunk et al., 1997; Lee et al., 2003; Tremblay et al., 2005; Turner and Rawling, 2001). However, the magnitude of enhancement is limited, usually less than a factor of 1.5 (Brunk et al., 1997; Tremblay et al., 2005). In this study, we found that the variations of pesticide sorption by Ca-SWy-2 in 0.1 M $CaCl_2$ ($I = 0.3$ M) are 0.8 to 1.7 factor of the sorption in 0.005 M $CaCl_2$ ($I = 0.015$ M); whereas sorption by K-SWy-2 within the same ionic strength range increased from 2 to 7 times. Using the empirical equations reported by Schwarzenbach et al. (1993), the reduced pesticide aqueous solubility was estimated to be less than a factor of 1.5 for the range of ionic strength used in this study. This is insufficient to cause the magnitude of enhanced sorption by K-SWy-2 observed in our study. Therefore, we conclude that the formation of K-smectite quasicrystals and possible shrinkage of interlayer distance resulting from increased KCl ionic strength are the primarily mechanisms responsible for enhanced pesticide sorption, while the salting-out effect plays a relatively minor role if any.

In summary, this study indicates that increasing KCl ionic strength results in enhanced pesticide sorption by K^+-saturated smectite plausibly because the increasing ionic strength promotes formation of K-smectite quasicrystals and reduces the basal spacings of clay interlayers, which in turn facilitate pesticide sorption. The result implies that the retention of pesticides by smectitic soils depends not only on soil intrinsic properties such as SOM and clay minerals but also on the surrounding environmental conditions such as ion type and strength in water. For the environments with high ionic-strength aqueous phases (e.g., estuaries, agricultural runoff, arid soils), particularly those containing K^+ and NH_4^+ salts, enhanced pesticide sorption by soils or sediments is expected, which alters pesticide environmental fate and transport. The amount of K^+, NH_4^+ salts present is not necessary to completely saturate the soil CEC sites, but needs to be sufficient to saturate the negative-charged sites associated with some clay layers or regions. In this scenario, clay demixing occurs leading to the formation of strong sorptive zones thereby enhancing pesticide sorption (Li et al., 2004b).

ACKNOWLEDGMENTS

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